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(54) Title: FIRE EXTINGUISHING METHODS UTILIZING HYDROFLUOROETHERS

(57) Abstract: Highly fluorinated, saturated and unsaturated hydrofluoroethers are efficient, economical, non-ozone-depleting fire
extinguishing agents used alone or in blends with other fire extinguishing agents in total flooding and portable systems.

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FIRE EXTINGUISHING METHODS UTILIZING HYDROFLUOROETHERS

FIELD OF THE INVENTION

5 The present invention is directed to hydrofluoroether fire extinguishing agents and methods for extinguishing fires using the hydrofluoroethers. More particularly, the present invention is directed to fire extinguishing agents and methods using saturated or unsaturated, fluorinated C₄ and/or C₅ hydrofluoroethers, and blends of one or more of the hydrofluoroethers with one or more other fire extinguishing agents.

10 BACKGROUND OF THE INVENTION AND PRIOR ART

The use of certain bromine, chlorine and iodine-containing halogenated chemical agents for the extinguishment of fires is common. These agents are in general thought to be effective due to their interference with the normal chain reactions responsible for flame propagation. The most widely
15 accepted mechanism for flame suppression is the radical trap mechanism proposed by Fryburg in *Review of Literature Pertinent to Fire Extinguishing Agents and to Basic Mechanisms Involved in Their Action*, NACA-TN 2102 (1950). The finding that the effectiveness of the halogens are on a molar basis in the order Cl < Br < I supports the radical trap mechanism, as reported by
20 Malcom in *Vaporizing Fire Extinguishing Agents*, Report 117, Dept. of Army Engineering Research and Development Laboratories, Fort Bevoir, VA, 1950 (Project- 8-76-04-003). It is thus generally accepted that compounds containing the halogens Cl, Br and I act by interfering with free radical or ionic species in

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the flame and that the effectiveness of these halogens is in the order $I > Br > Cl$. In addition, it is generally thought that to be effective as a fire extinguishing agent, a compound must contain Cl, Br or I.

The use of iodine-containing compounds as fire extinguishing agents has been avoided primarily due to the expense of their manufacture or due to toxicity considerations. Until very recently, the three fire extinguishing agents presently in common use were all bromine-containing compounds, Halon 1301 (CF_3Br), Halon 1211 (CF_2BrCl) and Halon 2402 ($BrCF_2CF_2Br$). The effectiveness of these three volatile bromine-containing compounds in extinguishing fires has been described in U.S. Pat. No. 4,014,799 to Owens. Although not employed commercially, certain chlorine-containing compounds are also known to be effective extinguishing agents, for example Halon 251 (CF_3CF_2Cl) as described by Larsen in U.S. Pat. No. 3,844,354.

Although the above named bromine or chlorine-containing Halons are effective fire fighting agents, those agents containing bromine or chlorine are asserted by some to be capable of the destruction of the earth's protective ozone layer. Also, because the agents contain no hydrogen atoms which would permit their destruction in the troposphere, the agents may also contribute to the greenhouse warming effect.

More recently, hydrofluorocarbons have been proposed as fire suppression, for example in U.S. Pat. No. 5,124,053. However, a disadvantage of these compounds is their relatively high global warming potential.

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It is therefore an object of this invention to provide a method for extinguishing fires that extinguishes fires as rapidly and effectively as the techniques employing Halon agents while avoiding the above-named drawbacks.

5 It is a further object of this invention to provide an agent for the use in a method of the character described that is efficient, economical to manufacture, and environmentally safe with regard to ozone depletion and greenhouse warming effects.

10 It is a still further object of this invention to provide blends of the new agents and other fire extinguishing agents that are effective and environmentally safe.

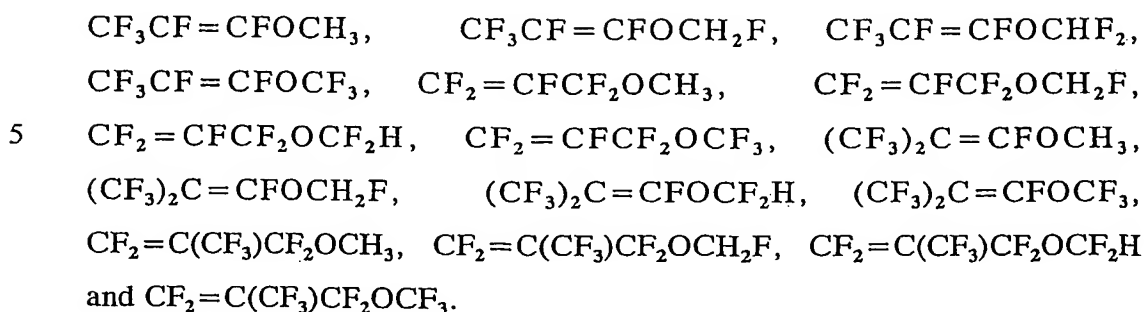
SUMMARY OF THE INVENTION

The foregoing and other objects, advantages and features of the present invention may be achieved by employing saturated or unsaturated, higher fluorinated hydrofluoroethers and blends thereof with other agents as fire
15 extinguishants for use in fire extinguishing methods and apparatus. More particularly, the method of this invention involves introducing to a fire a saturated or unsaturated, fluorinated C₄ or C₅ hydrofluoroether in a fire extinguishing concentration and maintaining such concentration until the fire is extinguished. Specific saturated, fluorinated C₄ or C₅ hydrofluoroethers of this
20 invention include:

$\text{CF}_3\text{CHF}\text{CF}_2\text{OCH}_3$, $\text{CF}_3\text{CHF}\text{CF}_2\text{OCH}_2\text{F}$, $\text{CF}_3\text{CHF}\text{CF}_2\text{OCF}_2\text{H}$,
 $\text{CF}_3\text{CHF}\text{CF}_2\text{OCF}_3$, $(\text{CF}_3)_2\text{CHCF}_2\text{OCH}_3$, $(\text{CF}_3)_2\text{CHCF}_2\text{OCH}_2\text{F}$,
 $(\text{CF}_3)_2\text{CHCF}_2\text{OCHF}_2$ and $(\text{CF}_3)_2\text{CHCF}_2\text{OCF}_3$.

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Specific unsaturated, fluorinated C₄ or C₅ hydrofluoroethers of the present invention include:



These hydrofluoroethers may be used alone, in admixture with
 10 each other or as blends with other fire extinguishing agents. Generally, the
 agents of this invention are employed at concentrations lying in the range of
 about 3 to 15%, preferably 5 to 10% in air, on a v/v basis. The agents of this
 invention are suitable for use in both total flooding and portable fire
 suppression applications. Suitable extinguishing agents ('blends') for admixture
 15 with the hydrofluoroethers include $\text{CF}_3\text{CHF}_2\text{CF}_3$, $\text{CF}_3\text{CF}_2\text{CF}_2\text{H}$, $\text{CF}_3\text{CH}_2\text{CF}_3$,
 $\text{CF}_3\text{CF}_2\text{H}$, and CF_3H .

The hydrofluoroethers of this invention may be produced via
 numerous routes. For example, $\text{CF}_3\text{CHF}_2\text{CF}_2\text{OCF}_2\text{H}$ may be prepared via a
 three step process comprising

- 20 (i) reaction of methanol with commercially available
 hexafluoropropene ($\text{CF}_3\text{CF}=\text{CF}_2$) in the presence of base to
 produce $\text{CF}_3\text{CHF}_2\text{CF}_2\text{OCH}_3$;
 (ii) chlorination of $\text{CF}_3\text{CHF}_2\text{CF}_2\text{OCH}_3$ with Cl_2 to produce
 $\text{CF}_3\text{CHF}_2\text{CF}_2\text{OCHCl}_2$; and

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- (iii) fluorination of $\text{CF}_3\text{CHF}\text{CF}_2\text{OCHCl}_2$ with HF to produce the final product $\text{CF}_3\text{CHF}\text{CF}_2\text{OCF}_2\text{H}$.

By further reacting with a strong base like sodium or potassium hydroxide the corresponding unsaturated C_4 or C_5 hydrofluoroethers may be prepared.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with the present invention, saturated and unsaturated C_4 and C_5 hydrofluoroethers have been found to be effective fire extinguishants at concentrations safe for use. However, because such hydrofluoroethers contain no bromine or chlorine, they have an ozone depletion potential of zero. Furthermore, since the compounds are characterized by short atmospheric lifetimes they are susceptible to breakdown in the lower atmosphere and hence do not pose a threat as greenhouse warming gasses.

Specific hydrofluoroethers useful in accordance with this invention are:

$\text{CF}_3\text{CHF}\text{CF}_2\text{OCH}_3$, $\text{CF}_3\text{CHF}\text{CF}_2\text{OCH}_2\text{F}$, $\text{CF}_3\text{CHF}\text{CF}_2\text{OCF}_2\text{H}$,
 $\text{CF}_3\text{CHF}\text{CF}_2\text{OCF}_3$, $(\text{CF}_3)_2\text{CHCF}_2\text{OCH}_3$, $(\text{CF}_3)_2\text{CHCF}_2\text{OCH}_2\text{F}$,
 $(\text{CF}_3)_2\text{CHCF}_2\text{OCHF}_2$, $(\text{CF}_3)_2\text{CHCF}_2\text{OCF}_3$, $\text{CF}_3\text{CF}=\text{CFOCH}_3$,
 $\text{CF}_3\text{CF}=\text{CFOCH}_2\text{F}$, $\text{CF}_3\text{CF}=\text{CFOCHF}_2$, $\text{CF}_3\text{CF}=\text{CFOCF}_3$,
 $\text{CF}_2=\text{CFCF}_2\text{OCH}_3$, $\text{CF}_2=\text{CFCF}_2\text{OCH}_2\text{F}$, $\text{CF}_2=\text{CFCF}_2\text{OCF}_2\text{H}$,
 $\text{CF}_2=\text{CFCF}_2\text{OCF}_3$, $(\text{CF}_3)_2\text{C}=\text{CFOCH}_3$, $(\text{CF}_3)_2\text{C}=\text{CFOCH}_2\text{F}$,
 $(\text{CF}_3)_2\text{C}=\text{CFOCF}_2\text{H}$, $(\text{CF}_3)_2\text{C}=\text{CFOCH}_3$, $\text{CF}_2=\text{C}(\text{CF}_3)\text{CF}_2\text{OCH}_3$,
 $\text{CF}_2=\text{C}(\text{CF}_3)\text{CF}_2\text{OCH}_2\text{F}$, $\text{CF}_2=\text{C}(\text{CF}_3)\text{CF}_2\text{OCF}_2\text{H}$ and $\text{CF}_2=\text{C}(\text{CF}_3)\text{CF}_2\text{OCF}_3$.

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These hydrofluoroethers may be used alone, in admixture with each other or as blends with other fire extinguishing agents. Generally, when a single hydrofluoroether of this invention is employed, concentrations lying in the range of about 3 to 15%, preferably 5 to 10% in air, on a v/v basis, are used; when employed in admixture, concentrations lying in the range of about 3 to 15%, preferably 5 to 10% in air, on a v/v basis, are used. Where the hydrofluoroethers of this invention are employed in admixture with other fire extinguishing agents ('blends'), the hydrofluoroethers desirably comprise of at least about 10 percent by weight of the blend, and the overall concentration of the blend lies in the range of about 3 to 15%, preferably 5 to 10% in air, on a v/v basis. The agents of this invention are suitable for use in both total flooding and portable fire suppression applications. Suitable extinguishing agents for admixture with the hydrofluoroethers include $\text{CF}_3\text{CHF}_2\text{CF}_3$, $\text{CF}_3\text{CF}_2\text{CF}_2\text{H}$, $\text{CF}_3\text{CH}_2\text{CF}_3$, $\text{CF}_3\text{CF}_2\text{H}$, and CF_3H .

15

The C_4 or C_5 hydrofluoroethers of this invention may be effectively employed at substantially any minimum concentrations at which fire may be extinguished, the exact minimum level being dependent on the particular combustible material, the particular hydrofluoroether and the combustion conditions. In general, however, best results are achieved where the hydrofluoroethers or mixtures and blends thereof are employed at a level of at least about 3% (v/v). Where hydrofluoroethers alone are employed, best results are achieved with agent levels of at least about 5% (v/v). Likewise, the maximum amount to be employed will be governed by matters of economics and potential toxicity to living things. About 15% (v/v) provides a convenient maximum concentration for use of hydrofluoroethers and mixtures and blends thereof in occupied areas. Concentrations above 15% (v/v) may be employed in unoccupied areas, with the exact level being determined by the particular combustible material, the hydrofluoroether (or mixture or blend thereof) chosen

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and the conditions of combustion. The preferred concentration of the hydrofluoroether agents, mixtures and blends in accordance with this invention lies in the range of about 5 to 10% (v/v).

Hydrofluoroethers may be applied using conventional application
5 techniques and methods used for Halons such as Halon 1301 and Halon 1211. Thus, these agents may be used in a total flooding fire extinguishing system in which the agent is introduced to an enclosed region (e.g., a room or other enclosure) surrounding a fire at a concentration sufficient to extinguish the fire. In accordance with a total flooding system apparatus, equipment or even rooms
10 or enclosures may be provided with a source of agent and appropriate piping, valves, and controls so as automatically and/or manually to be introduced an appropriate concentrations in the event that fire should break out. Thus, as is known to those skilled in the art, the fire extinguishant may be pressurized with nitrogen or other inert gas at up to about 600 psig at ambient conditions.

15 Alternatively, the hydrofluoroether agents may be applied to a fire through the use of conventional portable fire extinguishing equipment. It is usual to increase the pressure in portable fire extinguishers with nitrogen or other inert gasses in order to insure that the agent is completely expelled from the extinguisher. Hydrofluoroether containing systems in accordance with this
20 invention may be conveniently pressurized at any desirable pressure up to about 600 psig at ambient conditions.

The compounds of the present invention are nondestructive agents, and are especially useful where cleanup of other media poses a problem. Some of the applications of the hydrofluoroethers of this invention are the
25 extinguishing of liquid and gaseous fueled fires, the protection of electrical

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equipment, ordinary combustibles such as wood, paper and textiles, hazardous solids, and the protection of computer facilities, data processing equipment and control rooms.

5 The invention will be further described with reference to the following specific Examples. However it will be understood that these Examples are illustrative in nature and not restrictive in nature.

EXAMPLE 1

10 This example demonstrates the desirable "throw" obtainable with the fire suppression agents of the present invention when employed in portable ("streaming") applications. The throw is the distance the stream of agent can be discharged; the longer the throw the better, as this allows extinguishment without approaching the fire at too close a distance, which can lead to exposure of the operator to fire and toxic fumes from the combustion process.

15 A 150 mL SS cylinder was equipped with an inlet tube and a dip tube connected via an on/off valve to a delivery nozzle. The cylinder was charged with 50 grams of $\text{CF}_3\text{CHF}_2\text{OCF}_2\text{H}$ and then pressurized with nitrogen to the desired pressure. The cylinder contents were completely discharged and the throw distance noted (Table 1).

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TABLE 1**Throw vs. Pressure for $\text{CF}_3\text{CHF CF}_2\text{OCF}_2\text{H}$ System**

	Pressure, psig	Throw, feet
	25	10
5	80	15
	120	17
	150	18

EXAMPLE 2

10 This example demonstrates the extinguishment of Class B fires with the agents of the present invention. A 150 mL SS cylinder was equipped with an inlet tube and a dip tube connected via an on/off valve to a delivery nozzle. The cylinder was charged with 30 grams of $\text{CF}_3\text{CHF CF}_2\text{OCF}_2\text{H}$ and then pressurized with nitrogen to 120 psig. A 2 inch x 4 inch x 0.5 inch SS pan
15 was filled with 20 mL of methanol. The methanol was ignited and allowed to burn for 30 seconds; the agent was then discharged from a distance of 4 feet onto the fire. The methanol fire was extinguished in 1.5 seconds; a total of 16 grams of agent was discharged.

EXAMPLE 3

20 The method of Example 2 was employed with acetone, isopropanol and heptane fuels. All fires were rapidly extinguished (see Table 2).

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TABLE 2**Extinguishment with $\text{CF}_3\text{CHF}_2\text{OCF}_2\text{H}$**

	Fuel	Extinguishing Time, seconds	Agent discharged, grams
	acetone	2.0	25
5	isopropanol	1.5	21
	heptane	1.8	11

EXAMPLE 4

This example demonstrates the extinguishment of deep-seated Class A fires with the agents of the present invention. A 150 mL SS cylinder was equipped with an inlet tube and a dip tube connected via an on/off valve to a delivery nozzle. The cylinder was charged with 30 grams of $\text{CF}_3\text{CHF}_2\text{OCF}_2\text{H}$ and then pressurized with nitrogen to 120 psig. A wood crib was constructed of six layers of 6 inch x 2 inch by 0.125 inch strips of kiln dried fir, each layer consisting of 4 pieces. The crib was soaked with heptane, ignited, and allowed to burn for five minutes. The agent was then discharged onto the fire, resulting in rapid (< 2 seconds) extinguishment; a total of 25 grams of agent was discharged. Immediately after extinguishment the wood crib was cold to the touch, demonstrating the efficient suppression afforded by the agent.

WHAT IS CLAIMED IS:

1. A method for extinguishing a fire comprising the steps of introducing to the fire a fire extinguishing concentration of a composition comprising a compound selected from the group consisting of a saturated, fluorinated C₄ hydrofluoroether, a saturated, fluorinated C₅ hydrofluoroether, an unsaturated, fluorinated C₄ hydrofluoroether and an unsaturated, fluorinated C₅ hydrofluoroether and maintaining the concentration of the compound until the fire is extinguished.
2. The method of claim 1, wherein the compound is selected from the group consisting of CF₃CHF₂CF₂OCH₃, CF₃CHF₂CF₂OCH₂F, CF₃CHF₂CF₂OCF₂H, CF₃CHF₂CF₂OCF₃, (CF₃)₂CHCF₂OCH₃, (CF₃)₂CHCF₂OCH₂F, (CF₃)₂CHCF₂OCHF₂, (CF₃)₂CHCF₂OCF₃, CF₃CF=CFOCH₃, CF₃CF=CFOCH₂F, CF₃CF=CFOCHF₂, CF₃CF=CFOCF₃, CF₂=CFCF₂OCH₃, CF₂=CFCF₂OCH₂F, CF₂=CFCF₂OCF₂H, CF₂=CFCF₂OCF₃, (CF₃)₂C=CFOCH₃, (CF₃)₂C=CFOCH₂F, (CF₃)₂C=CFOCF₂H, (CF₃)₂C=CFOCH₃, CF₂=C(CF₃)CF₂OCH₃, CF₂=C(CF₃)CF₂OCH₂F, CF₂=C(CF₃)CF₂OCF₂H and CF₂=C(CF₃)CF₂OCF₃.

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3. The method of claim 1, wherein the compound is selected from the group consisting of $\text{CF}_3\text{CHF}\text{CF}_2\text{OCH}_3$, $\text{CF}_3\text{CHF}\text{CF}_2\text{OCH}_2\text{F}$, $\text{CF}_3\text{CHF}\text{CF}_2\text{OCF}_2\text{H}$; $\text{CF}_3\text{CHF}\text{CF}_2\text{OCF}_3$, $(\text{CF}_3)_2\text{CHCF}_2\text{OCH}_3$, $(\text{CF}_3)_2\text{CHCF}_2\text{OCH}_2\text{F}$, $(\text{CF}_3)_2\text{CHCF}_2\text{OCHF}_2$, $(\text{CF}_3)_2\text{CHCF}_2\text{OCF}_3$.

5 4. The method of claim 1, wherein the compound is employed at a level of at least about 3 % (v/v).

5. The method of claim 1, wherein the compound is employed in a total flooding system.

6. The method of claim 1, wherein the compound is
10 employed in a portable extinguishing system.

7. The method of claim 1, wherein the composition comprises a blend with other fire extinguishing agents.

8. The method of claim 7, wherein the other fire extinguishing agents are selected from the group consisting of $\text{CF}_3\text{CHF}\text{CF}_3$,
15 $\text{CF}_3\text{CF}_2\text{CF}_2\text{H}$, $\text{CF}_3\text{CH}_2\text{CF}_3$, $\text{CF}_3\text{CF}_2\text{H}$, and CF_3H .

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9. A fire extinguishing agent comprising a compound selected from the group consisting of $\text{CF}_3\text{CHF}_2\text{CF}_2\text{OCH}_3$, $\text{CF}_3\text{CHF}_2\text{CF}_2\text{OCH}_2\text{F}$, $\text{CF}_3\text{CHF}_2\text{CF}_2\text{OCF}_2\text{H}$, $\text{CF}_3\text{CHF}_2\text{CF}_2\text{OCF}_3$, $(\text{CF}_3)_2\text{CHCF}_2\text{OCH}_3$, $(\text{CF}_3)_2\text{CHCF}_2\text{OCH}_2\text{F}$, $(\text{CF}_3)_2\text{CHCF}_2\text{OCF}_2\text{H}$, $(\text{CF}_3)_2\text{CHCF}_2\text{OCF}_3$, $\text{CF}_3\text{CF}=\text{CFOCH}_3$, $\text{CF}_3\text{CF}=\text{CFOCH}_2\text{F}$, $\text{CF}_3\text{CF}=\text{CFOCHF}_2$, $\text{CF}_3\text{CF}=\text{CFOCF}_3$, $\text{CF}_2=\text{CFCF}_2\text{OCH}_3$, $\text{CF}_2=\text{CFCF}_2\text{OCH}_2\text{F}$, $\text{CF}_2=\text{CFCF}_2\text{OCF}_2\text{H}$, $\text{CF}_2=\text{CFCF}_2\text{OCF}_3$, $(\text{CF}_3)_2\text{C}=\text{CFOCH}_3$, $(\text{CF}_3)_2\text{C}=\text{CFOCH}_2\text{F}$, $(\text{CF}_3)_2\text{C}=\text{CFOCF}_2\text{H}$, $(\text{CF}_3)_2\text{C}=\text{CFOCH}_3$, $\text{CF}_2=\text{C}(\text{CF}_3)\text{CF}_2\text{OCH}_3$, $\text{CF}_2=\text{C}(\text{CF}_3)\text{CF}_2\text{OCH}_2\text{F}$, $\text{CF}_2=\text{C}(\text{CF}_3)\text{CF}_2\text{OCF}_2\text{H}$ and $\text{CF}_2=\text{C}(\text{CF}_3)\text{CF}_2\text{OCF}_3$.

10. A method of making $\text{CF}_3\text{CHF}_2\text{CF}_2\text{OCF}_2\text{H}$ comprising the steps of
- (i) reacting methanol with hexafluoropropene in the presence of base to produce $\text{CF}_3\text{CHF}_2\text{CF}_2\text{OCH}_3$;
 - (ii) chlorinating $\text{CF}_3\text{CHF}_2\text{CF}_2\text{OCH}_3$ with Cl_2 to produce $\text{CF}_3\text{CHF}_2\text{CF}_2\text{OCHCl}_2$; and
 - (iii) fluorinating $\text{CF}_3\text{CHF}_2\text{CF}_2\text{OCHCl}_2$ with HF to produce $\text{CF}_3\text{CHF}_2\text{CF}_2\text{OCF}_2\text{H}$.

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11. A method of making a saturated, fluorinated C₄ or C₅ hydrofluoroether comprising the steps of

- (i) reacting a C₁ alcohol with a fluorinated C₃ or C₄ alkene in the presence of a base to form a first reaction product;
- 5 (ii) chlorinating the first reaction product with Cl₂ to form a second reaction product; and
- (iii) fluorinating the second reaction product with HF to form a saturated, fluorinated C₄ or C₅ hydrofluoroether.

12. The method of claim 11, wherein the base is selected
10 from the group consisting of sodium and potassium hydroxide.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A62D C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 730 894 A (MINOR BARBARA HAVILAND) 24 March 1998 (1998-03-24)	1-4, 7, 9
Y	column 2, line 1 column 3, line 54 - column 6, line 33 column 9, line 50 - line 60; claims 1, 6, 7	8
X	WO 96 40834 A (DU PONT) 19 December 1996 (1996-12-19) page 5, line 9; claims 16, 17	1-3, 9
Y	WO 93 24586 A (DU PONT) 9 December 1993 (1993-12-09) page 3, line 6 - line 14 page 7, line 22 - line 28; claims 1, 3, 4	8
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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(54) Title: FIRE EXTINGUISHING METHODS UTILIZING HYDROFLUOROETHERS

(57) Abstract: Highly fluorinated, saturated and unsaturated hydrofluoroethers are efficient, economical, non-ozone-depleting fire extinguishing agents used alone or in blends with other fire extinguishing agents in total flooding and portable systems.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5730894	A	24-03-1998	WO 9739081 A1	23-10-1997
WO 9640834	A	19-12-1996	EP 0830436 A1	25-03-1998
			JP 10506926 T	07-07-1998
			WO 9640834 A1	19-12-1996
WO 9324586	A	09-12-1993	US 5605882 A	25-02-1997
			AT 177137 T	15-03-1999
			AU 4250093 A	30-12-1993
			BR 9306614 A	08-12-1998
			CN 1082088 A	16-02-1994
			DE 69323743 D1	08-04-1999
			DE 69323743 T2	09-09-1999
			EP 0642560 A1	15-03-1995
			ES 2130267 T3	01-07-1999
			JP 7507342 T	10-08-1995
			MX 9303120 A1	30-06-1994
			WO 9324586 A1	09-12-1993
			US 5648016 A	15-07-1997
			US 6416683 B1	09-07-2002
			US 5779931 A	14-07-1998
US 6023002	A	08-02-2000	AU 7691198 A	09-08-1999
			EP 1051381 A1	15-11-2000
			JP 2002501035 T	15-01-2002
			WO 9937598 A1	29-07-1999
WO 0105468	A	25-01-2001	AU 6223600 A	05-02-2001
			EP 1261398 A2	04-12-2002
			WO 0105468 A2	25-01-2001
			US 6478979 B1	12-11-2002
US 5562861	A	08-10-1996	US 5611210 A	18-03-1997
			US 5695688 A	09-12-1997
			AT 193903 T	15-06-2000
			AU 681640 B2	04-09-1997
			AU 6358794 A	26-09-1994
			BR 9405991 A	26-12-1995
			CA 2157567 A1	15-09-1994
			CN 1122606 A ,B	15-05-1996
			DE 69424935 D1	20-07-2000
			EP 0687287 A1	20-12-1995
			JP 8507524 T	13-08-1996
			RU 2140955 C1	10-11-1999
			WO 9420588 A1	15-09-1994
			US 5605647 A	25-02-1997
			US 5685915 A	11-11-1997
			US 5444102 A	22-08-1995
			US 5674451 A	07-10-1997
			US 5716549 A	10-02-1998
US 2730543	A	10-01-1956	NONE	
EP 0562858	A	29-09-1993	US 5278342 A	11-01-1994
			US 5196600 A	23-03-1993
			AT 186527 T	15-11-1999
			AU 669604 B2	13-06-1996
			AU 5777894 A	22-09-1994

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/44256

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document; with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 023 002 A (CHEBURKOV YURI ET AL) 8 February 2000 (2000-02-08) column 1, line 21 - line 30 column 3, line 20 - line 32 column 7, line 63 - column 8, line 5 column 11, line 8 - line 11 ----	1,2,7,9
P,X	WO 01 05468 A (3M INNOVATIVE PROPERTIES CO) 25 January 2001 (2001-01-25) page 9, line 12 - line 25; table 1 ----	1,4,7
P,A	FUKAYA H ET AL: "Fire extinguishing ability of perfluoroalkylamines and perfluoroethers evaluated by a small cup burner method" JOURNAL OF FLUORINE CHEMISTRY, ELSEVIER SEQUOIA, LAUSANNE, CH, vol. 106, no. 2, December 2000 (2000-12), pages 143-146, XP004219156 ISSN: 0022-1139 the whole document ----	1-9
A	US 5 562 861 A (NIMITZ JONATHAN S ET AL) 8 October 1996 (1996-10-08) column 14, line 25 - line 50; claims 1,11,13,14; table 4 ----	1-9
Y	US 2 730 543 A (RENDALL JOHN L ET AL) 10 January 1956 (1956-01-10) column 1, line 44 - line 52 column 4, line 39 - line 45 ----	11,12
Y	EP 0 562 858 A (HAMPSHIRE CHEMICAL CORP) 29 September 1993 (1993-09-29) claims 1-18; example 1 ----	11,12
A	PATENT ABSTRACTS OF JAPAN vol. 1995, no. 04, 31 May 1995 (1995-05-31) & JP 07 025803 A (AGENCY OF IND SCIENCE & TECHNOL; OTHERS: 04), 27 January 1995 (1995-01-27) abstract ----	10-12
A	US 3 557 294 A (GILBERT EVERETT E ET AL) 19 January 1971 (1971-01-19) column 2, line 57 - line 61 ----	10-12
A	US 3 943 256 A (REGAN BERNARD M) 9 March 1976 (1976-03-09) column 2, line 17 - line 23 -----	10-12

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 01/44256

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☒ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/44256

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
EP 0562858	A	BR 9401152 A	01-11-1994	
		CA 2118828 A1	16-09-1994	
		CN 1100711 A ,B	29-03-1995	
		DE 69326970 D1	16-12-1999	
		DE 69326970 T2	29-06-2000	
		EP 0562858 A1	29-09-1993	
		ES 2139626 T3	16-02-2000	
		JP 6298693 A	25-10-1994	
JP 07025803	A	27-01-1995	JP 2589917 B2	12-03-1997
US 3557294	A	19-01-1971	NONE	
US 3943256	A	09-03-1976	BE 813867 A1	16-08-1974
		FR 2233986 A1	17-01-1975	
		GB 1469423 A	06-04-1977	
		US 3976788 A	24-08-1976	
		ZA 7403055 A	27-08-1975	

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-9

A method for extinguishing a fire and a fire extinguishing agent comprising a saturated, fluorinated C4 or C5 hydrofluoroether, or an unsaturated, fluorinated C4 or C5 hydrofluoroether

2. Claims: 10-12

A method of making saturated, fluorinated C4 or C5 hydrofluoroether